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# Geologic carbon sources may confound ecosystem carbon balance estimates: Evidence from a semiarid steppe in the southeast of Spain

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[1] At a semiarid steppe site located in the SE of Spain, relatively large CO<sub>2</sub> emissions were measured that could not be attributed to the ecosystem activity alone. Since the study site was located in a tectonically active area, it was hypothesized that a part of the measured CO<sub>2</sub> was of geologic origin. This investigation included a survey of soil CO<sub>2</sub> efflux, together with carbon isotope analyses of the CO<sub>2</sub> in the soil atmosphere, soil CO<sub>2</sub> efflux (i.e., Keeling plots), groundwater and local thermal springs. These measurements confirmed the hypothesis of degassing from geologic sources. In areas with local faults and ancient volcanic structures, soil CO<sub>2</sub> efflux rates were significantly higher (i.e., up to 6.3 and 1.4  $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ ) than measurements in a comparable site that was some distance from fault sites (means of 1.0 and 0.43  $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$  in March and June, respectively). The CO<sub>2</sub> concentration in the soil atmosphere at the eddy covariance site reached 0.14% v/v at 0.70 m soil depth with a <sup>13</sup>C-enriched isotopic composition ( $\delta^{13}\text{C}$  from  $-10.2\text{‰}$  to  $-16.6\text{‰}$ ), consistent with the isotopic composition of the soil CO<sub>2</sub> efflux estimated by Keeling plots (i.e.,  $-16.6\text{‰}$ ). <sup>13</sup>C-enriched CO<sub>2</sub> also occurred in local aquifers, and there was evidence of degassing from deep crust and mantle at regional scale by the helium isotopic ratio in spring waters located about 30 km (R/Ra: 0.12) and 200 km (R/Ra: 0.95) NW of the eddy covariance site. This study highlights the importance of considering CO<sub>2</sub> sources of geologic origin when assessing the net ecosystem carbon balance of sites that may possibly be affected by circulation of such CO<sub>2</sub>-rich fluids.

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## 1. Introduction

[2] As a consequence of increasing concern about the impact of climate change on functioning of ecosystems, there has recently been considerable interest in understanding the variables that control carbon cycling, particularly in terrestrial ecosystems [Le Quéré *et al.*, 2009]. As a result, substantial methodological advances have been made, increasing confidence in our estimates of the contributions of terrestrial

ecosystems to the global carbon balance [Ciais *et al.*, 2008; Le Quéré *et al.*, 2009; Beer *et al.*, 2010]. As a result, extensive data sets of fluxes of carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) from a range of ecosystems are now available [e.g., Batjes and Bridges, 1994; Bonan, 1995; Law *et al.*, 2002; U.S. Environmental Protection Agency (EPA), 2010, 2012].

[3] However, the majority of studies presuppose that virtually all the exchanges of CO<sub>2</sub> and CH<sub>4</sub> between terrestrial ecosystems and the atmosphere are the consequences of biologic processes resulting from photosynthesis, plant respiration, microbial activity and animal respiration. This approach may be inappropriate in situations where ecosystems may release gases of geologic origin, i.e., gases that have originated in the subsoil rocks and subterranean structures, ranging from the lithosphere to the Earth's mantle [see review by Kerrick, 2001].

[4] It is well known that CO<sub>2</sub> of geologic origin is released to the atmosphere not only by volcanoes, but also diffusely from the soil in geothermal areas or over tectonic faults, independently of the surface ecosystem. Geologic faults generally act as pathways for migration to the Earth's surface of gas originating by deep (typically >1 km) thermo-metamorphism of carbonate rocks or mantle degassing

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**Table 1.** Main Characteristics of the Balsablanca Eddy Covariance Site [After Rey *et al.*, 2011]

Characteristic	Description
Longitude	2°1'58"W
Latitude	36°56'30"N
Altitude (m)	208
Orientation	NW
Slope (%)	2–6
Average annual temperature (°C)	18
Maximum summer temperature (°C)	34
Average annual rainfall (mm)	200
Mean annual atmospheric pressure (kPa)	99
Mean annual relative humidity (%)	69.3
Vegetation	Steppe alpha grass
Soil type <sup>a</sup>	Mollic Lithic Leptosol (Calcaric)
Soil texture class	Sandy loam
Soil depth (cm)	0–30
Clay (%)	16.1
Silt (%)	22.8
Sand (%)	61.1
Bulk density (g cm <sup>-3</sup> )	1.25
Mean annual soil temperature (°C)	21.9
Mean annual soil water content (%)	13.8

<sup>a</sup>IUSS Working Group WRB [2006].

[e.g., Barnes *et al.*, 1978; Grace and van Gardingen, 1997; Chiodini *et al.*, 1999; Etiope, 1999; Kerrick, 2001; Mörner and Etiope, 2002]. This deep and widespread geologic CO<sub>2</sub> should not be confused with that produced locally by weathering (dissolution) of shallow calcareous rocks, which may be involved in the carbon balance of ecosystems located on karstic environments [e.g., Kowalski *et al.*, 2008; Serrano-Ortiz *et al.*, 2009]. Geologic CO<sub>2</sub> has been found to occur extensively in soils throughout wide areas characterized by grassland or woodland ecosystems in Europe and USA, even without evidence at the Earth surface of geothermal manifestations and far from volcanic systems [e.g., Gregory and Durrance, 1985; Hinkle, 1990; Chiodini *et al.*, 1999; Etiope, 1999; Klusman *et al.*, 2000; Lewicki and Brantley, 2000; Klusman, 2005]. These “hidden” geologic sources may release several types of endogenous gases (e.g., CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, He) to the atmosphere, some of which can contribute to the net ecosystem carbon exchange of terrestrial ecosystems.

[5] While CO<sub>2</sub> is the most important carbon-bearing gas in geothermal-volcanic areas, geologic CH<sub>4</sub> emissions may be relevant in sedimentary basins with petroleum production [Etiope and Klusman, 2010]. Indeed, geo-CH<sub>4</sub> sources are extremely important at global scale, representing the second largest natural CH<sub>4</sub> source (at least 60 Tg y<sup>-1</sup>) [Etiope, 2012] after wetlands, and about 10% of the total CH<sub>4</sub> emissions [Etiope *et al.*, 2008; EPA, 2010]. Earth's degassing is considered to be a relatively minor CO<sub>2</sub> source globally (probably in the order of 600–1000 Tg CO<sub>2</sub> y<sup>-1</sup> i.e., ~2%–3% of the anthropogenic sources and 10% of the carbon source resulting from deforestation and land-use change, and about 18% of the current terrestrial sink [Mörner and Etiope, 2002; Pan *et al.*, 2011]. Both geo-CH<sub>4</sub> and geo-CO<sub>2</sub> may, however, affect surface ecosystem fluxes on wide areas and confound local scale carbon budgets attributed to biologic activity leading to inaccurate estimates. An example of such a phenomenon involving CH<sub>4</sub> may be represented by emission of geologic gas in agricultural rice paddies in Japan which can be confused with biologic gas emissions [Etiope

*et al.*, 2011]. An example involving geo-CO<sub>2</sub> is presented in this paper.

[6] A recent study carried out with the aim of quantifying the carbon, water and energy ecosystem fluxes using the eddy covariance technique in a natural grassland ecosystem in southeastern Spain reported relatively large CO<sub>2</sub> emissions over the dry period that could not be attributed to the vegetation activity alone [Rey *et al.*, 2012]. Anomalous ecosystem CO<sub>2</sub> emissions and interannual patterns were observed at the Balsablanca eddy covariance site that suggested the presence of other nonbiologic carbon sources. As a consequence, we could not apply standard partitioning techniques to derive photosynthesis and respiration [Reichstein *et al.*, 2005; Lasslop *et al.*, 2010]. After examination of the study area, we concluded that the site of Balsablanca is located in a geothermal basin very close to a tectonic fault system of regional importance (the Carboneras Fault). This then led to the hypothesis of a geologic contribution to the CO<sub>2</sub> efflux from the soil [Rey *et al.*, 2012].

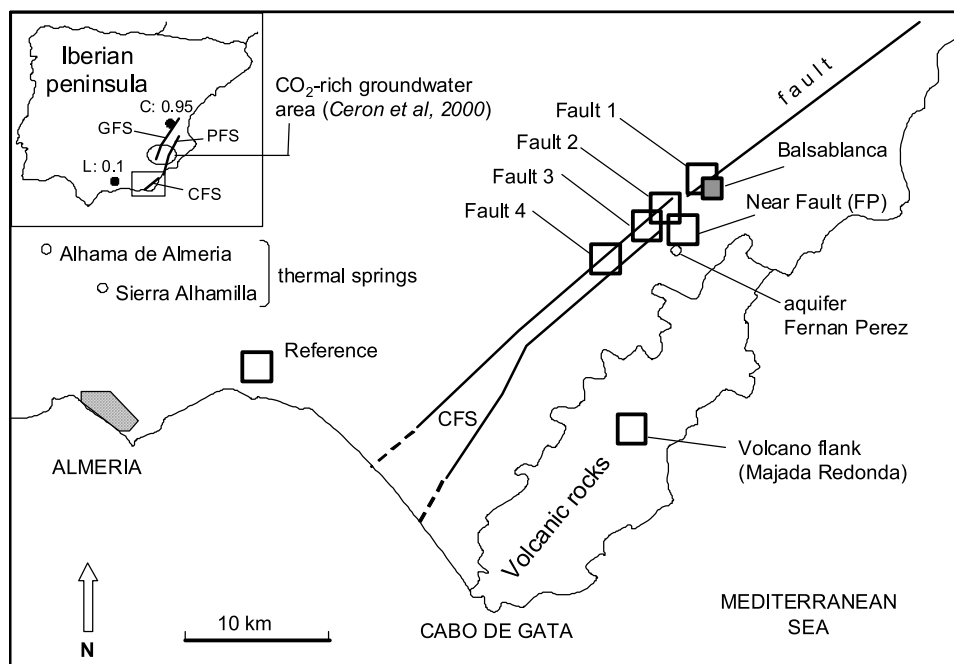
[7] Here, we verify this hypothesis through an investigation that includes a soil CO<sub>2</sub> efflux survey, carbon isotopic analyses of CO<sub>2</sub> in the soil atmosphere (at the eddy covariance site), aquifers and natural water springs located approximately 30 km southwest of Balsablanca (part of the same geologic system). Isotopic composition of helium (<sup>3</sup>He/<sup>4</sup>He), a tracer of deep-origin gas, was analyzed in a natural water spring and compared with literature data of other springs in the same geologic region (onshore Alboran Basin). In addition, Keeling plots, a widely used method to determine the carbon isotope composition of ecosystem respiration [Pataki *et al.*, 2003], were used to assess the stable carbon isotopic ratio of soil CO<sub>2</sub> efflux. All data confirm the presence in the soil of CO<sub>2</sub> of geologic origin, which may confound assessments of the local ecosystem carbon balance that can be attributed to ecosystem activity.

## 2. Material and Methods

### 2.1. Site Description

[8] The study site of Balsablanca is located in the Cabo de Gata Natural Park, in the province of Almería (Andalusia), in southeastern Spain (36°56'26.0"N, 2°01'58.8"W). The climate in this area is subtropical, dry, and semiarid with a mean annual precipitation of 250 mm and a mean annual temperature of approximately 18°C (Table 1). It is characterized by prolonged summer droughts (from May to September), and infrequent and random rainfall events when the vegetation is mostly inactive [Rey *et al.*, 2011]. Annual potential evapotranspiration is approximately 1390 mm (nearby meteorological station of Níjar). Precipitation mostly occurs in spring and autumn with strong interannual variation and random events.

[9] The site is equipped with meteorological and eddy covariance towers designed to measure the exchange of carbon, water, and energy between the ecosystem and the atmosphere (part of the CARBOEUROPE and FLUXNET networks of flux sites since May 2006). The ecosystem is a natural grassland characterized by open vegetation-free areas (65% ground coverage), dominated by *Stipa tenacissima*. The dominant soils are classified as Lithic leptosols (calcaric) [IUSS Working Group WRB, 2006], and are thin, of variable depth (on average 10 cm), alkaline (pH > 8), saturated



**Figure 1.** Location map of soil CO<sub>2</sub> efflux measurement sites (squares) and groundwater sampling in thermal springs and aquifer (small circles). The small Iberia map shows the location of degassing sites west and northeast of the investigated area (rectangle): L: Lanjarón, with helium isotopic ratio R/Ra: 0.1; C: Cofrentes, with R/Ra: 0.95 [Pérez *et al.*, 1996]. GFS: Guedalentin Fault System; PFS: Palomares Fault System [Ceron *et al.*, 2000]. The CO<sub>2</sub>-rich groundwater area refers to the sites with <sup>13</sup>C-enriched carbon waters similar to those of the aquifer near Balsablanca (see text). Fault and volcanic rock locations are after Aguirre *et al.* [2006].

in carbonates with a moderate stone content and with frequent rock outcrops (additional details of the site are given by Rey *et al.* 2011, 2012).

[10] Geologically, the site of Balsablanca is in the Betic Cordilleras, at the western margin of the Cabo de Gata volcanic complex of Miocene age (last volcanic episode is about 7.5 Ma old), formed as a consequence of extensional processes related to the development of the Alboran Basin after the Alpine collision between the African and Eurasian plates [Sanz de Galdeano, 1990; Martín *et al.*, 2009]. The Balsablanca site is located exactly over the Carboneras Fault System (CFS; Figure 1), one of the three main regional tectonic faults of southeast Spain (the other two are the Palomares, and Guadalentin sinistral strike-slip faults) producing a shear zone with crustal thinning (“rifting”) and regional seismicity [Sanz de Galdeano *et al.*, 1995]. The area represents a rift basin related to the formation of other European similar rifts, like the Rhine basin in Germany and the Rhone and Algero-Provençal basins in France [Sanz de Galdeano, 1990]. The CFS produced a large-scale deformation zone with relevant fracturation of the Miocene sedimentary and volcanic rocks. The adjacent ancient volcano hosted hydrothermal systems with several fluid emission points, including fumaroles (Cinto, Los Tolles), today extinct, located at about 13 km southwest of Balsablanca. The contemporary geothermal condition of the Cabo de Gata area is evidenced by the relatively high heat flow, 84 mW m<sup>-2</sup> (against an average of 65 mW m<sup>-2</sup> for the Iberian mainland) measured in a well about 20 km southwest of Balsablanca [Fernández *et al.*, 1998].

[11] The stratigraphic rock sequence in the Balsablanca area is formed by outcrops of old Quaternary alluvial fans, calcareous conglomerates and sands (Pliocene), marine carbonates (Messinian and Tortonian) and volcanic rocks (Tortonian) at about 80–100 m below the ground, overlying the Betic carbonatic Mesozoic basement [Martín *et al.*, 2009].

## 2.2. Soil CO<sub>2</sub> Efflux Survey

[12] We postulated that soil CO<sub>2</sub> efflux rates were likely to be higher or anomalous in areas associated with geologic gas exhalation. We therefore tested whether we could detect higher soil CO<sub>2</sub> efflux rates associated with proximity to the fault and an ancient volcano area and compared those rates with rates measured in a reference “background” location far from the volcano fault system, but with similar vegetation (alpha grass) and soil substrate (calcaric Lithic leptosol), as shown in Figure 1.

[13] Because soil chamber methods provide a flux measurement at small spatial scale, numerous measurements were made to characterize both spatial trends and variability of fluxes at both sites. The so-called reference background site, is an area supposedly not affected by any geothermal activity in the ground, where we would expect the measured soil CO<sub>2</sub> efflux rates to be solely the result of biologic activity or soil respiration. A total of 200 soil CO<sub>2</sub> efflux measurements were made by static closed-chamber methods on two occasions: in March (when the vegetation is still active) and in June 2011 (the vegetation is mostly dormant and soil respiration is strongly limited by water shortage [Rey *et al.*, 2011]). The measurements were made in five

different locations along the Carboneras fault, at the top of an ancient volcano (the Majada Redonda volcanic caldera), at the eddy covariance tower site of Balsablanca, and at the reference background site. Four sites along the Carboneras fault (Faults 1–4) refer to alpha grass ecosystems located exactly in correspondence with the main Carboneras fault line, based on published geologic maps, satellite images and field recognition of morphological tectonic scarps and outcrops. The “Near Fault” site (close to Fernán Pérez village) is along a minor morphological scarp of probable tectonic origin, 500 m south of the main fault line (in correspondence with Fault 2 site).

[14] All measurements were done on similar alpha grass ecosystems but on bare soil patches between plants (at least 50 cm from a plant), and on the same vegetation type as at the Balsablanca site (*Stipa tenacissima*). In March, a 10 dm<sup>3</sup> closed chamber was connected to West Systems flux meter with Licor CO<sub>2</sub> analyzer (West Systems, Pontedera, Italy) [Etioppe *et al.*, 2011] and in June a 3.5 dm<sup>3</sup> closed chamber connected to a soil respiration system EGM-4 (PP Systems, Hitchin, UK) was used. We intended to use the same instrument in both occasions but it was not possible because of a malfunction problem with the EGM-4 instrument at the first sampling period. However, both sets of equipment were calibrated against each other for consistency and soil CO<sub>2</sub> efflux rates corrected accordingly using a regression between both estimates ( $n = 10$ ,  $R^2 = 0.90$ ). All measurements were made between 10.00 h and 14.00 h during several days to avoid diurnal fluctuations and to obtain a range of environmental conditions: growing season in March soon after a rainy period (soil volumetric water content above 5% and air temperature below 20°C and thus with the vegetation still active) and a dry period in June (soil volumetric water content below 5% and air temperature above 20°C, with the vegetation mostly dormant, as shown by Rey *et al.* [2011]). The exact location of each measurement point was recorded with a GPS. Soil temperature at 3.5 cm depth was measured with a digital thermometer and soil volumetric water content with a portable theta probe (ML2x, Devices Ltd., Cambridge, UK) at the time of each soil CO<sub>2</sub> efflux measurement. To test whether soil CO<sub>2</sub> efflux rates measured in both periods differed between sites, a single analysis of variance at a probability of 5% was done (PROC ANOVA) using SAS statistical software 9.2. (SAS Software, SAS Institute, Cary, N.C., USA).

### 2.3. Keeling Plots

[15] In order to determine the carbon isotopic composition of soil CO<sub>2</sub> efflux we used the Keeling plot approach as described by Pataki *et al.* [2003]. This approach uses a two-component mixing model that consists of the carbon isotope ratio of CO<sub>2</sub> ( $\delta^{13}\text{C}$ ) released and that in the background atmosphere. The intercept of a linear regression of  $\delta^{13}\text{C}$  of atmospheric CO<sub>2</sub> versus  $1/[\text{CO}_2]$  (where  $[\text{CO}_2]$  is the mole fraction of CO<sub>2</sub>) provides an estimate of the  $\delta^{13}\text{C}$  of the soil CO<sub>2</sub> efflux (CR).

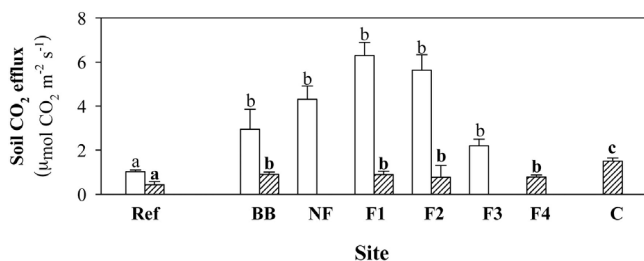
[16] For this purpose, we designed 15 clear opaque chambers with soil collars made of PVC (20 cm in diameter and 10 cm high). The soil collars were inserted 3 cm into the ground one day before each measurement campaign. The chambers were designed with a sealed T-connector at the top to allow air sampling during each measurement campaign.

The lids were placed at time 0 and a first sample of air from a chamber was taken with a 50 cm<sup>3</sup> LUER LOK syringe with an insulin needle; the sample was injected under slight pressure into a 20 cm<sup>3</sup> vial previously left under vacuum. Five samples from each chamber were taken every 15 min, so that all five samples per chamber were taken in 75 min. Chamber dimensions and measuring time interval were estimated based on previous soil CO<sub>2</sub> efflux rates at the site to ensure a large enough CO<sub>2</sub> gradient (75 ppmv, as advised by Pataki *et al.* [2003]) and linearity between  $[\text{CO}_2]$  and  $\delta^{13}\text{C}$  [Takahashi and Liang, 2007]. The glass vials were sealed with rubber stop-cocks and a hot glue gun until analyses. Septum-capped vials have been tested and proven to be suitable for air transport [Glatzel and Well, 2008]. The vials, including vials with standards, were taken to the laboratory in the *Centro Nazionale delle Ricerche* at Porano (Italy) and analyzed for CO<sub>2</sub> concentration and  $\delta^{13}\text{C}$  with a Gas Chromatography-Isotopic Ratio Mass Spectrometry (ISOPRIME mod. JB287, GV Instruments, Manchester, UK) connected to a multiflow Gilson 222XL auto-sampler. We determined the evolution rate and isotopic composition [ $\delta^{13}\text{C}(\text{‰})$ :  $\delta^{13}\text{C} = 1,000 [(R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}]$  (‰), where:  $R = {}^{13}\text{C}/{}^{12}\text{C}$ ] of the CO<sub>2</sub> from the soil sample. The CO<sub>2</sub> evolution rate and  $\delta^{13}\text{C}$  of the evolved CO<sub>2</sub> were calculated from the change over time in CO<sub>2</sub> concentration and  $\delta^{13}\text{C}$  of the CO<sub>2</sub> in the sampled vials.

[17] Samples were taken on the 3–4 June 2011. We placed the soil chambers in the most representative soil covers at the site [Rey *et al.*, 2011] laid out in five plots each one with three soil cover types: under plant, biologic soil crust and bare soil. Soil temperature and soil volumetric water content measured at 3.5 cm was recorded at the time of each measurement adjacent to each chamber as described above. To ensure further that vial usage, overpressurization and storage did not influence the results; we carefully evaluated each step (including transport from the site in Spain to the lab in Italy) by comparing all measurements with a standard of known concentration and carbon isotopic composition in the mass spectrometer (standard deviation less than 0.02‰). Since there were no statistically significant differences between the regression lines of individual replicates ( $P < 0.05$ ), we fitted all measured points for each soil cover type to a single regression line in order to calculate the intercept for each soil cover—i.e., the  ${}^{13}\text{C}$  of the CO<sub>2</sub> released under each soil cover type—and compared the regression lines for any significant differences among the slopes and intercepts (general linear models (GLM) in SAS statistical software).

### 2.4. Sampling and Analyses of Soil-Air and Gas Dissolved in Aquifers and Springs

[18] Seven soil-gas samples (0.70 m deep) were collected at two points (P1 and P2) at the Balsablanca site by inserting into the soil a metallic probe (3 cm in diameter and 100 cm long), that was sealed at the top and left to equilibrate with the soil atmosphere for a day. A syringe and silicon tube equipped with a T-valve, were used to reduce atmospheric air contamination during sampling. The first sample at P1 was stored in a 150 cm<sup>3</sup> glass tube equipped with two stop-cocks, for molecular compositional analyses. The other six samples (three in P1 and three in P2) were stored in 12 cm<sup>3</sup> evacuated vials for CO<sub>2</sub> and  $\delta^{13}\text{C}_{\text{CO}_2}$  analyses.



**Figure 2.** Bar plot of soil CO<sub>2</sub> efflux rates measured at the different locations along the Carboneras fault (F1, F2, F3, F4), near fault (NF), at the eddy covariance tower site (BB), at an ancient volcano caldera (C) and a reference site (Ref) measured in March (white area) and June (striped area). Bars represent the mean ( $\pm 1$ SE) of all measuring points at each site ( $n = 15$ – $20$ ). Bars with different letters (a, b, c) of the same period are statistically significantly different (ANOVA,  $P < 0.05$ ).

[19] Additionally, three water samples were collected from a public well drilled into the main aquifer of the Fernán Pérez and Balsablanca area. The well reaches a depth of 140 m corresponding to carbonate/volcanic rocks ( $36^{\circ}54'50.46''\text{N}$ ,  $12^{\circ}03'59.73''\text{W}$ ; see Figure 1). 250 cm<sup>3</sup> water samples were taken and sealed with a rubber stopper and kept in a fridge until analysis.

[20] Four water samples were also collected at two thermal springs, located about 30 km southwest of Balsablanca, at Sierra Alhamilla ( $36^{\circ}58'57.6''\text{N}$ ,  $2^{\circ}23.8'32.99''\text{W}$ ) and Alhama de Almería ( $36^{\circ}57'26.73''\text{N}$ ,  $2^{\circ}34'12.27''\text{W}$ ). Water was stored in 250 cm<sup>3</sup> glass bottles. CO<sub>2</sub>,  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{13}\text{C}_{\text{TDIC}}$  (Total Dissolved Inorganic Carbon) analyses in six soil-gas and five water samples (two from the springs and three from the aquifer) were done by the Stable Isotope Facility of the University of California, Davis.  $\delta^{13}\text{C}_{\text{CO}_2}$  was measured using a ThermoScientific PreCon-GasBench system interfaced to a Thermo Scientific Delta V Plus isotope ratio mass spectrometer (Thermo Scientific, Bremen, Germany). Two laboratory standards, calibrated against NIST 8545, were analyzed every 10 samples. Long-term standard deviation was 0.02‰.  $\delta^{13}\text{C}_{\text{TDIC}}$  was analyzed using a Surveyor HPLC coupled to a ThermoFinnigan Delta Plus Advantage isotope ratio mass spectrometer (Thermo Scientific, Bremen, Germany) through a LC Isolink interface. Two laboratory standards (lithium carbonate dissolved in degassed deionised water and a deep seawater reference sample, both calibrated against NIST 8545), were analyzed every 10 samples.

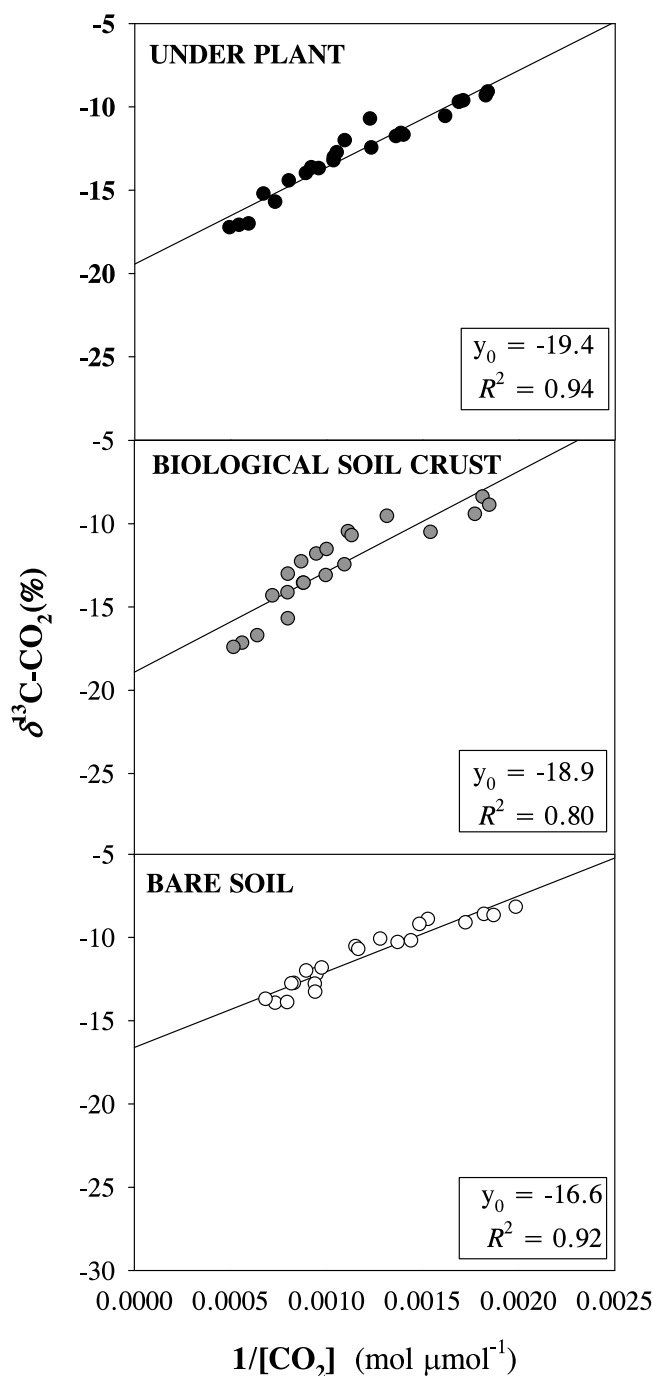
[21] Compositional analyses of soil-air, including N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, CO, He, and isotopic composition of helium in a water spring (Sierra Alhamilla), were done by the Fluid Chemistry Laboratory of Istituto Nazionale di Geofisica e Vulcanologia di Palermo. The dissolved gas was extracted in the laboratory after attainment of equilibrium (at constant temperature) between water samples and a known volume of host, high-purity gas (argon), injected into the sampling bottle (as described by Capasso and Inguaggiato [1998]). The analytical determinations were carried out using a Perkin Elmer 8500 gas chromatograph equipped with a double detector (TCD-FID), with argon as the carrier gas. Helium isotope analyses were done on gas fractions extracted following the same procedure as for the gas chromatography.

The samples were then purified following standard procedures [see Sano and Wakita, 1988]. The isotopic analyses of the purified helium fraction were performed by a static vacuum mass spectrometer (GVI5400TFT) that allows for simultaneous detection of <sup>3</sup>He and <sup>4</sup>He-ion beams, thereby keeping the <sup>3</sup>He/<sup>4</sup>He error of measurement to very low values. Typical uncertainties in the range of low-<sup>3</sup>He samples are within 5%. Helium isotopic ratio is expressed in the R/Ra notation, which is the <sup>3</sup>He/<sup>4</sup>He ratio between sample and atmospheric air ( $=1.4 \times 10^{-6}$ ); the ratio has been corrected for atmospheric contamination (based on the <sup>4</sup>He/<sup>20</sup>Ne ratio) [Hilton, 1996].

### 3. Results and Discussion

#### 3.1. Soil CO<sub>2</sub> Efflux

[22] Environmental conditions differed between the two periods, with optimal conditions for plant and soil activity in March, whereas conditions were most likely minimal during the dry period in June [Rey et al., 2011]. Soil CO<sub>2</sub> efflux rates were always higher in March than in June, including measurements on bare soil (where biologic activity is minimal compared to the heterotrophic and autotrophic respiration in patches beneath plants with high fine root density and soil organic matter content). However, the tendency for higher soil CO<sub>2</sub> efflux rates on sites associated with proximity to the fault and ancient volcano was found in both measurement periods. Rates of soil CO<sub>2</sub> efflux measured at all the fault sites and at the volcanic caldera were systematically higher than the rates measured at the reference site, with rates ranging from 6.3 to 2.2  $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$  and from 1.4 to 0.77  $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$  in March (when fault sites were significantly different from the reference site,  $P < 0.05$ ) and June (when fault sites were significantly different from the reference site,  $P < 0.001$ ), respectively (Figure 2). In June, the highest mean soil CO<sub>2</sub> efflux was recorded at the ancient caldera. At the reference site, soil CO<sub>2</sub> efflux rates ranged from 1.0 to 0.4  $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$  in March and June, respectively. At the Balsablanca site, soil CO<sub>2</sub> efflux rates were intermediate with an average value of 3.0 and 0.9  $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$  in March and June, respectively. The measured soil CO<sub>2</sub> efflux rates at Balsablanca are consistent with those measured previously on bare soil at the site [Rey et al., 2011] but higher than expected based on rates typically occurring on bare soils under similar environmental conditions in semiarid grasslands [e.g., Conant et al., 2000; Maestre and Cortina, 2006; Carbone et al., 2008]. In particular, soil CO<sub>2</sub> efflux rates measured along the fault are higher than soil respiration rates reported in semiarid grasslands, although still low compared to the mean biologic CO<sub>2</sub> efflux from soils, which ranges from 0.2 to 21 g C m<sup>-2</sup> d<sup>-1</sup> [e.g., Raich and Tufekcioglu, 2000; Bond-Lamberty and Thomson, 2010]. Since wind is the main driver of the short-term net ecosystem carbon balance (NECB) at the eddy covariance site of Balsablanca where CO<sub>2</sub> effluxes of up to 15  $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$  were measured over the dry period in concurrence with strong winds [Rey et al., 2012], it is likely that closed static chambers may preclude some of the CO<sub>2</sub> from deep origins to be released, so that soil CO<sub>2</sub> efflux rates were underestimated. However, we were primarily concerned with the relative comparison between sites and would, therefore, still expect the observed differences



**Figure 3.** Keeling plots of soil  $\text{CO}_2$  efflux at three soil covers: under *Stipa* plants, biologic soil crusts and bare soil ( $n = 5$ ) in June 2011. Samples were collected from each chamber with at least 75 ppmv  $\text{CO}_2$  change between successive samples over a 75-min period. Measurements were made at noon, when soil temperatures averaged  $25^\circ\text{C}$ . The Keeling plot calculations are given in the text. Isotope ratios are plotted against the inverse of  $\text{CO}_2$  concentration.

between different locations. Surface winds and atmospheric dispersion, in particular, are very effective at diluting  $\text{CO}_2$  micro-seepage fluxes [Oldenburg et al., 2003]. Since most of the  $\text{CO}_2$  produced by biologic activity, particularly in the very shallow soils (Table 1), is generated close to the soil

surface [Rey et al., 2008] the geologic  $\text{CO}_2$  component coming from deeper layers would be the most underestimated component when using closed chamber methods.

[23] Since all measurements were made on bare soil far from any plant and under very dry conditions, particularly over the dry season, we would expect minimal biologic contribution to the measured soil  $\text{CO}_2$  effluxes. Indeed, we observed relatively low rates at the reference steppe site compared to other ecosystems [Bond-Lamberty and Thomson, 2010]. Instead, soil  $\text{CO}_2$  efflux measured within fault areas were larger than expected based on previous long-term soil  $\text{CO}_2$  efflux records measured under similar environmental conditions at the Balsablanca site [Rey et al., 2011] and those measured in other ecosystems in the area located far from the fault and ancient volcanic caldera [Oyonarte et al., 2012]. Although the absolute values may be low compared to other ecosystems, and even more compared to other active geothermal areas where large soil  $\text{CO}_2$  emissions have been reported [e.g., Werner and Brantley, 2003; Chiodini et al., 2008], the relative contribution to carbon emissions in this ecosystem may be considerable as indicated by the relatively large  $\text{CO}_2$  emissions measured during dry periods by eddy covariance at the Balsablanca site [Rey et al., 2012]. Indeed, in a follow-up study in which we have partitioned net ecosystem carbon balance into biologic and geologic components, it has been estimated that approximately half of the  $\text{CO}_2$  emitted comes from geologic sources (A. Rey et al., Partitioning estimates of net ecosystem carbon balance into biological and geological sources in a semiarid steppe ecosystem in the southeast of Spain, manuscript in preparation, 2012).

### 3.2. $\delta^{13}\text{C}$ of Soil $\text{CO}_2$ Efflux

[24] Based on the mixing model approach described in the Material and Methods section [Pataki et al., 2003], we calculated an averaged  $\delta^{13}\text{C-R}$  (of the three soil covers at the eddy covariance site) to be  $-18.3\text{‰}$  ( $\pm 0.51$ ). Within each soil type, variability was low and replicated measurements of  $\delta^{13}\text{C-R-soil}$  were statistically indistinguishable so all replicates were used to fit a single regression line for each soil cover (Figure 3). In contrast, the  $\delta^{13}\text{C-R-soil}$  of  $\text{CO}_2$  efflux from soils differed among soil cover types as expected ( $P < 0.001$ ). In June 2011, the  $\delta^{13}\text{C-R-soil}$  was  $-19.4$  ( $\pm 0.39$ ),  $-18.9$  ( $\pm 0.76$ ) and  $-16.6$  ( $\pm 0.40$ )‰ for soil  $\text{CO}_2$  efflux measured under plant, biologic soil crust and bare soil, respectively (Figure 3). The intercept was significantly different among soil covers ( $P < 0.001$ ). This pattern of  $\delta^{13}\text{C-R-soil}$  increasing with plant proximity is reasonable given that the contribution of depleted carbon from organic sources is expected to increase with proximity to plants (most roots and soil organic matter are found below plants) [see Rey et al., 2011]. However, all values confirmed the presence of a nonbiologic component of  $\text{CO}_2$  in the respired  $\text{CO}_2$ . The  $\delta^{13}\text{C}$  value of present atmospheric  $\text{CO}_2$  is close to  $-8\text{‰}$  [Bowling et al., 2008]. The  $\delta^{13}\text{C}$  composition of  $\text{CO}_2$  respired from plant roots is isotopically depleted relative to the atmosphere as a result of isotopic fractionation during photosynthesis and will have an isotopic composition between  $-24$  to  $-38\text{‰}$  in  $\text{C}_3$  plants [Pataki et al., 2003]. When most of the  $\text{CO}_2$  released comes from biologic sources, one would expect the carbon isotopic signal of the respired soil  $\text{CO}_2$  to be close to that of the plant material [Hungate

**Table 2.** CO<sub>2</sub> Concentration and  $\delta^{13}\text{C}$  Values (CO<sub>2</sub> or T<sub>DIC</sub>) in Soil-Air (0.7 m Deep) at the Balsablanca Eddy Covariance Tower Site, in the Local Aquifer of Fernán Pérez and in the Closest Thermal Springs (Including a Water Sample With Helium Concentration and Isotopic Ratio)

Site	Type	CO <sub>2</sub> (ppmv)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰, VPDB <sup>a</sup> )	$\delta^{13}\text{C}_{\text{T}_{\text{DIC}}}$ (‰, VPDB)	T <sub>DIC</sub> (mM)	He (ppmv)	R/Ra
Balsablanca P1 ( <i>n</i> = 1)	Soil-air	1400	−10.2				
Balsablanca P1 ( <i>n</i> = 3)	Soil-air	555–588	−16.6 ± 0.19				
Balsablanca P2 ( <i>n</i> = 3)	Soil-air	436–521	−14.5 ± 0.01				
Fernán Pérez ( <i>n</i> = 3)	Aquifer		−14.1 ± 0.29 <sup>b</sup>	−6.1 ± 0.3	1.80 ± 0.36		
Alhama de Almería spring	Spring	25038	−12.1				
Sierra Alhamilla spring	Spring	19595	−16.4			91	0.12

<sup>a</sup>VPDB: Vienna Pee Dee Belemnite standard.<sup>b</sup>Recalculated values based on the procedure by Mook *et al.* [1974].

*et al.*, 1997; Werner and Gessler, 2011]. Foliar  $\delta^{13}\text{C}$  values of *Stipa tenacissima* measured in the same area are on average −24‰ [Maestre and Cortina, 2006; Armas *et al.*, 2009]. Instead, when other carbon sources are present, the isotopic signal of the CO<sub>2</sub> released should be  $^{13}\text{C}$  enriched. Note that as a result of fractionation during diffusion (*ca.* −4.4‰) [Amundson *et al.*, 1998], the soil respired CO<sub>2</sub> is depleted in  $\delta^{13}\text{C}$  relative to the soil CO<sub>2</sub> (Table 2). This is not apparent under steady state conditions, in which case soil derived CO<sub>2</sub> becomes enriched by +4.4‰ and the  $\delta^{13}\text{C}$  of soil-respired CO<sub>2</sub> approaches that of the source organic material [Dörr and Münich, 1987; Cerling *et al.*, 1991].

[25] In most cases, respiration processes predominantly operate in the soil zone. Therefore, the isotopic composition of CO<sub>2</sub> beneath the soil should be less affected by isotopic composition of the soil gases. In particular, numerous studies have reported CO<sub>2</sub> carbon isotopic (*i.e.*,  $\delta^{13}\text{C}$ –CO<sub>2</sub>) compositions down vertical soil gas profiles, demonstrating that CO<sub>2</sub> undergoes significant isotopic fractionation during its diffusive pathway through the soil atmosphere both in volcanic-hydrothermal degassing areas [Camarda *et al.*, 2007], where a deep CO<sub>2</sub> source is present, and in vegetated areas [Amundson *et al.*, 1998; Cerling *et al.*, 1991], where the soil CO<sub>2</sub> flux is the result of biogenic sources alone. The  $\delta^{13}\text{C}$  values of this CO<sub>2</sub> will be similar to that of the organic source mass and may not vary significantly from values of the soil-respired CO<sub>2</sub>.

### 3.3. CO<sub>2</sub> in Soil-Air at Balsablanca

[26] The concentration of CO<sub>2</sub> detected at a depth of 0.70 m in the soil at Balsablanca ranged from 436 to 1400 ppmv (Table 2). The 1400 ppmv CO<sub>2</sub> sample had 77.8% N<sub>2</sub>, 19.1% O<sub>2</sub>, 2 ppmv CH<sub>4</sub> and 5 ppmv He.  $\delta^{13}\text{C}_{\text{CO}_2}$  ranged from −10.2‰ (in the 1400 ppmv sample) to −16.1‰ (555 ppmv), with an average value of −14‰. This is approximately 6‰ lower than atmospheric CO<sub>2</sub> and 10 to 24‰ higher than typical biologic CO<sub>2</sub> released in soil respiration [Pataki *et al.*, 2003]. The  $\delta^{13}\text{C}$  signature of CO<sub>2</sub> derived from geothermal sources (*e.g.*, magmatic or metamorphic sources) typically ranges from −2‰ to −6‰ [Faure, 1986] and will mix with CO<sub>2</sub> derived from C<sub>3</sub> plants. The 1400 ppmv concentration is considerable given that the sample was taken from a depth with no mineral soil [Rey *et al.*, 2011]. This value is, however, rather low for areas with deep CO<sub>2</sub> degassing [*e.g.*, Etiope, 1999; Etiope *et al.*, 1999; Williams-Jones *et al.*, 2000]. However, taken together with the  $\delta^{13}\text{C}$  of soil air, which was similar to that of soil water and the thermal spring nearby, this value further suggests that some CO<sub>2</sub> occurring in the soil is

inorganic, derived from deep carbon sources. These may include CO<sub>2</sub> produced by thermo-metamorphism of carbonate rocks and mantle material (typically producing  $\delta^{13}\text{C}$  of about 0‰ and −6.5‰ respectively [Sano and Marty, 1995]. Values of  $\delta^{13}\text{C}$  similar to those of Balsablanca are known to occur in soils affected by deep-origin CO<sub>2</sub> degassing in several countries, *e.g.*, in central Italy [Klusman *et al.*, 2000]. In particular, values in the range of −17‰ to −5‰ have been considered to represent mixing between biologic CO<sub>2</sub> (<−17‰) and hydrothermal CO<sub>2</sub> (>−5‰) [Chiodini *et al.*, 2008]. The measured Balsablanca values of  $\delta^{13}\text{C}_{\text{CO}_2}$  are in agreement with values that have been derived from Keeling plots, as reported in Section 3.2.

### 3.4. CO<sub>2</sub> Dissolved in Groundwater and Helium at Sierra Alhamilla

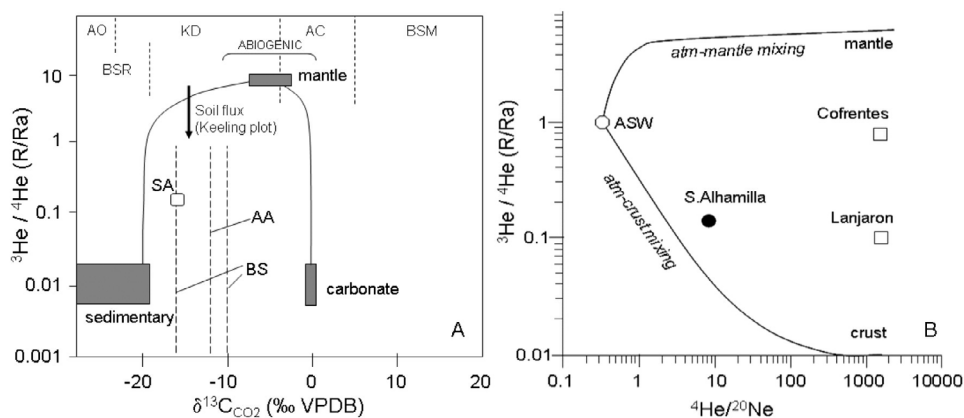
[27] The average  $\delta^{13}\text{C}_{\text{T}_{\text{DIC}}}$  value of three water samples of the local aquifer was −6.1‰. This is similar to the values of between −8.1‰ and −3.8‰, reported for groundwater located in the Guadalentín Fault System (GFS), which is a rift basin similar to the study area, about 35 km north of Balsablanca [Cerón *et al.*, 2000] (Figure 1). It is known that in aquifers affected by even low CO<sub>2</sub> degassing, CO<sub>2</sub> should be dominantly present in the aqueous phase as dissolved inorganic carbon (T<sub>DIC</sub>, *i.e.*, CO<sub>2</sub>(aq), H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>−</sup>, and CO<sub>3</sub><sup>2−</sup>). With the increasing degassing of CO<sub>2</sub>, DIC also increases.

[28] The values of  $\delta^{13}\text{C}$ –CO<sub>2</sub> (−14.1‰) recalculated on the basis of equilibrium constants of the dissolved carbon species (with isotope enrichment factors for the CO<sub>2</sub> gas–HCO<sub>3</sub> and the CO<sub>2</sub> gas–CO<sub>2</sub> aq. systems [Mook *et al.*, 1974]) are similar to those measured in the soil-air at Balsablanca and lie within the range of those measured in the thermal springs. The two thermal springs located about 30 and 40 km west of Balsablanca in fact showed  $\delta^{13}\text{C}_{\text{CO}_2}$  values of −12.1‰ and −16.4‰, with concentrations of CO<sub>2</sub> in the extracted gas-phase of up to 25000 ppmv. The  $\delta^{13}\text{C}_{\text{CO}_2}$  values are consistent with those of the soil and the aquifers, and this suggests that mixing between the biologic, meteorologic and geologic carbon pools is a widespread and general process in the area.

[29] The helium isotopic ratio (R/Ra) measured in the gas extracted from the Sierra Alhamilla spring was 0.12. This is associated to a <sup>4</sup>He/<sup>20</sup>Ne ratio of about 8, which is about 28 times higher than the atmospheric ratio, and thus indicates negligible atmospheric contamination.

[30] The R/Ra versus  $\delta^{13}\text{C}_{\text{CO}_2}$  plot (Figure 4a), traditionally used to estimate crustal versus mantle components of CO<sub>2</sub>





**Figure 4.** He isotopic ratio R/Ra versus  $\delta^{13}\text{C}_{\text{CO}_2}$  (A) and versus  $^4\text{He}/^{20}\text{Ne}$  (B). SA: Sierra Alhamilla spring; AA: Alhama de Almería spring; BS: Balsablanca soil.  $\text{CO}_2$  isotope zonation modified after Etiope *et al.* [2011]. AO, aerobic hydrocarbon oxidation; KD, kerogen decarboxylation; AC, alteration of marine carbonates; BSM, biodegradation and secondary methanogenesis; BSR, biologic soil respiration; ASW, air-saturated water. Cofrentes and Lanjarón springs data are from Pérez *et al.* [1996]. Vertical arrow indicates the  $\delta^{13}\text{C}_{\text{CO}_2}$  value derived by the Keeling plot of Figure 3.

[Sano and Marty, 1995], showed that the Sierra Alhamilla spring is close to the mixing line between sedimentary and mantle end-members. The stable carbon isotopic composition of  $\text{CO}_2$  exhaled from the soil derived by the Keeling plots is within the range of the values measured in the soil-air. However, all the values are higher than the range expected for biologic soil respiration (BSR). The helium isotopic ratio then suggests a deep gas source, with a dominant crustal component and minor (about 1%) mantle signal (Figure 4b). A similar R/Ra value, 0.1, has been reported for  $\text{CO}_2$ -rich waters at Lanjarón (Granada), about 100 km southwest of Balsablanca (Figure 1) [Pérez *et al.*, 1996]. Higher values, 0.95, were found at Cofrentes [Pérez *et al.*, 1996], which is 200 km northeast of Balsablanca. This last value suggests that about 10% of helium has a mantle origin. The increase of the mantle signal from south to north, passing through the Balsablanca area, reflects a younger and more active (seismic) tectonic activity toward the northern sector of the southeast Spain rift [Pérez *et al.*, 1996]. It is known, then, that  $\text{CO}_2$  degassing may increase or decrease in relation to seismicity [e.g., Bräuer *et al.*, 2003], and consequently the geo- $\text{CO}_2$  component in the Balsablanca soil may change over time, thus reflecting the tectonic activity of CFS.

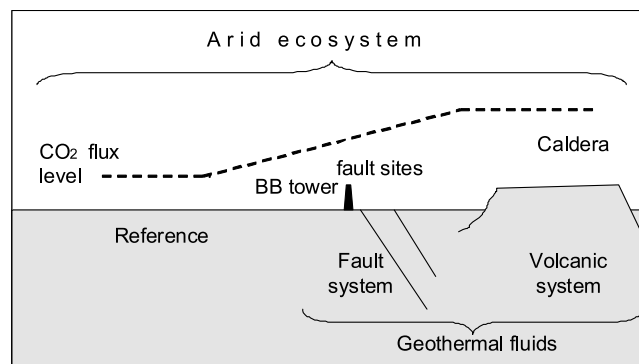
#### 4. Conclusions and Recommendations for Future Work

[31] The hypothesis proposed initially by Rey *et al.* [2012], regarding the occurrence of endogenous  $\text{CO}_2$  released from beneath the steppe ecosystem under study, is supported here by a combination of soil  $\text{CO}_2$  efflux measurements and carbon isotopic analyses of soil air and groundwater.

[32] In correspondence with local faults and ancient volcanic structures, soil  $\text{CO}_2$  efflux rates were higher than those measured far from fault sites regardless of the measuring period (Figure 5); the soil  $\text{CO}_2$  efflux at the eddy covariance site, accidentally positioned over a large fault system, reached concentrations of 0.14% v/v at 0.70 m depth with a  $^{13}\text{C}$ -enriched isotopic composition ( $\delta^{13}\text{C}$  from  $-10.2\text{‰}$  to

$-16.6\text{‰}$ ), consistent with the values derived from Keeling plots (i.e.,  $-16.6\text{‰}$  in bare soil).  $^{13}\text{C}$ -enriched carbon also occurred in local aquifers, and signals of degassing from deep crust and even mantle were detected at regional scale by the helium isotopic ratio in thermal spring waters. The geologic origin of  $\text{CO}_2$ , is probably not then related to weathering processes acting on relatively shallow calcareous rocks or subterranean cavity ventilation (as hypothesized by Kowalski *et al.* [2008] and Serrano-Ortiz *et al.* [2009] for some karstic areas), but is most likely related to deeper, regional geothermal fluid circulation systems connected to the ancient volcanism of Cabo de Gata. As also suggested by the relatively high geothermal heat flow and the helium isotopic composition in springs, the relevant  $\text{CO}_2$  production mechanism may be similar to that of typical geothermal  $\text{CO}_2$ -degassing areas, widespread on all continents (i.e., thermo-metamorphism of deep carbonate rocks and degassing from the mantle) [e.g., Mörrer and Etiope, 2002; Chiodini *et al.*, 2008].

[33] 1) In an earlier study of the steppe ecosystem [Rey *et al.*, 2012], it was estimated that the NECB ranged from



**Figure 5.** Schematic model of geo- $\text{CO}_2$ /soil- $\text{CO}_2$  mixing in relation to geologic factors of the Cabo de Gata area.

65.7 to 143.6 g C m<sup>-2</sup> y<sup>-1</sup>, suggesting that the steppe ecosystem could be an appreciably large carbon source to the atmosphere. The present investigation has shown that even in areas where emissions of geologic CO<sub>2</sub> are not immediately evident, the contribution of “hidden” endogenous sources of CO<sub>2</sub> may be of major importance to the ecosystem carbon budget.

[34] 2) Given the low content of soil organic matter and small standing biomass at the site, an initial interpretation was that the ecosystem under study was highly unsustainable. The present investigation has clarified that a significant part of the carbon released did not result from ecosystem activity but was derived from geologic sources.

[35] 3) When ecosystems are on geologically active or geothermal areas, additional sources of carbon do contribute negatively to the net ecosystem carbon balance and must be taken into account when estimating the net ecosystem carbon exchange with the atmosphere.

[36] 4) By not taking into account geologic CO<sub>2</sub> sources, considerable errors in the estimates of the NECB attributed to vegetation activity may result. A further study aimed at separating the geologic from the biologic components of the CO<sub>2</sub> released, has estimated an average contribution of geologic CO<sub>2</sub> to the NECB of 55% (Rey et al., manuscript in preparation, 2012).

[37] 5) At local ecosystem scale, an appropriate initial geologic site inspection is recommended in relation to carbon budget objectives. On national, continental and global scales, carbon emission data sets from geographic areas potentially affected by geologic gas releases should be the object of further examination.

[38] 6) Thus the FLUXNET community should be aware of geologic CO<sub>2</sub> and CH<sub>4</sub> carbon sources when planning field measurements and should take these into account when estimating the net ecosystem carbon balance of vegetation, particularly in tectonically active areas, but more widely when modeling regional, continental and global carbon budgets.

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